

## COAL LIQUEFACTION KINETICS

Shaojie Wang, Keyu Wang, He Huang, Michael T. Klein and William H. Calkins\*  
Department of Chemical Engineering  
University of Delaware, Newark, Delaware 19716

Key words: kinetics, coal liquefaction, modelling

### Introduction

Understanding the mechanisms of uncatalyzed direct coal liquefaction by means of reaction kinetics has been a long sought goal. Curran et al. in 1967 (1) and Wiser in 1968 (2) and Neavel in 1976 (3) measured the rates of liquefaction of various coals and postulated a free radical mechanism to explain the data obtained. The kinetics as determined by these and other workers is described in detail by Gorin in Chapter 27 of Elliott's Second Supplementary Volume to the Chemistry of Coal Series (4). However, it has been well known that most coals contain some material extractable by organic solvents. The solvents used in direct coal liquefaction would of course be expected to also extract soluble material as well as effect the liquefaction reaction. If the extractable material were a significant quantity in the coal, it would seriously affect the kinetics. Cassidy et al. (5,6) used a stirred autoclave with a sampling port at the bottom in their kinetic studies. They observed that hot charging the coal rapidly formed an oil which they considered to originate predominantly from the "guest component", i.e., extractables, in the lignite they studied. Also, the free radical nature of the liquefaction process would be expected to produce secondary reaction products which would complicate the kinetics as well as lead to retrograde products.

With this background, it seemed important to measure the kinetics of direct liquefaction at very short contact times where the extractables would be quickly removed and secondary reactions due to the free radical nature of the liquefaction would be minimized. By the use of a special Short Contact Time Batch Reactor (SCTBR), we have been able to show that direct coal liquefaction occurs both thermally and catalytically in at least two separate and distinct stages: an extraction stage and a slower breakdown and liquefaction of the coal macromolecules themselves (7,8). With this equipment, it is possible to study the kinetics of each stage and to measure the kinetic parameters of each. The kinetics of two coals (Illinois #6 bituminous and Wyodak-Anderson subbituminous coals) investigated at reaction times from 10 s to 60 min are reported in this paper.

### Experimental

**Apparatus.** The Short Contact Time Batch Reactor was used to carry out the liquefactions. The design and operation of the reactor system including a schematic diagram have been described elsewhere (9,10). In brief, a 30 cm<sup>3</sup> reactor is constructed of 3/4" o.d. stainless steel tubing of approximately 12" length with wall thickness of approximately 0.433". The 21 ft lengths of coiled stainless tubing used for both the preheater and precoolers are 1/4" o.d. with wall thickness of 0.035". The reactor system is capable of containing up to 17 MPa (2500 psi) pressure at temperatures of up to 500°C.

In operation, both the empty preheater and the reactor are immersed in a Technic IFB-52 fluidized sand bath. They are brought up to the reaction temperature prior to the start of the reaction. High pressure hydrogen or nitrogen gas provided the driving force to deliver the slurry mixture of coal-solvent or coal-solvent-catalyst under study from a small blow case at ambient temperature into the empty reactor through the hot preheater tubing. Hydrogen or nitrogen gas was then bubbled through the reactor from the bottom to provide the agitation needed in the liquefaction reaction. The degree of agitation was controlled by the exit gas flow rate from the top of the reactor. In the case of running under hydrogen pressure, the gas bubbles were also used to supply the hydrogen for the liquefaction reaction.

The temperature of the reactants (ca. 30 g) initially at ambient temperature, approach the desired reaction temperature to within 5-8°C during the transport process (approximately 0.3 seconds) and reaches the predetermined reaction temperature within 30 seconds. At a preselected time, the high pressure gas is again used to drive the reactor contents from the reactor into a cold receiver through the precooler. Both receiver and precooler are immersed in a water bath. Quenching of the product mixture to about 25°C is achieved during the transport time of about 0.3 seconds.

**Coal Studied.** Illinois #6 bituminous and Wyodak-Anderson subbituminous coals from the Argonne Premium Coal Sample program were investigated in this study. Proximate and elemental analyses, together with other analytical data, of these coals are available in the User's Handbook for the Argonne Premium Coal Sample program (11).

**Workup Procedures of the Reaction Products.** The product mixtures were filtered and the solid residues washed with cold fresh tetralin thoroughly and dried in a vacuum oven with a nitrogen purge at 105°C for 48 hours. The filter cake was then rinsed with methylene

chloride and dried in a vacuum oven with a nitrogen purge at 105°C for 12 hours. The solid residue and the liquid filtrate were analyzed separately by various procedures.

**Thermogravimetric Analysis.** The thermogravimetric analyzer was a Model 51 TGA (TA Instruments, New Castle, Delaware). The TGA which was run on liquefaction residues provided a measure of the amount of volatile matter (VM), fixed carbon (FC) and ash. The mineral matter of the coal was shown to accumulate in the coal residue and not in the coal liquids. Ash in the residue was therefore used to calculate the conversion using the formula:

$$\text{Conversion (wt\%)} = \left(1 - \frac{A_0}{A_s}\right) \times 100\% \quad (1)$$

where  $A_0$  and  $A_s$  are the weight fractions of ash (derived from the coal mineral matter) in a control sample and in the liquefaction residue, respectively.

The volatile matter (VM) in the residue turned out to be only a function of the reaction time and temperature. The fixed carbon (FC), however, is a measure of the retrograde processes occurring during the liquefaction and the kinetics of the FC formation could be followed by TGA.

## Results and Discussion

**Liquefaction Conversion vs Time.** Figure 1 shows conversion vs time curves for Illinois #6 coal without added catalyst in tetralin (8 to 1 tetralin to coal weight ratio) at four temperatures and 1000 psig nitrogen atmosphere. There are several stages in the liquefaction as shown by these curves. There is an initial rapid conversion which is due to the extraction of soluble matter into the tetralin. This is followed by a pseudo-induction period during which little conversion appears to occur. This is not due to the build up of any intermediates such as free radicals as shown by ESR spectroscopy (12). Actually it is due to the simultaneous ending of the extraction stage and the slow conversion of the coal structure to liquid products. As the temperature increases, the extent of the extraction process increases and the pseudo-induction period becomes shorter. At still higher temperatures, particularly in the presence of a strong hydrogenation catalyst, the induction period becomes almost undetectable.

In nitrogen, there is little increase in conversion to liquid products above 408°C, although the reaction mixture is changing rapidly. We have shown that the volatile matter (VM) content decreases steadily as the time and temperature increases. However, the fixed carbon (FC) values increase dramatically at higher temperature, resulting in decreased yield of tetralin soluble materials (8).

Similar conversion curves are obtained for the liquefaction of the Wyodak-Anderson subbituminous coal in tetralin (8 to one tetralin to coal by weight)(8). These curves show the characteristic stages of extraction, induction period and coal liquefaction similar to the Illinois #6 coal.

Conversion vs time curves for both Illinois #6 and Wyodak Anderson coals in tetralin in the presence of hydrogen and added catalysts will be presented with a kinetic analysis in a future paper.

**Kinetic Analysis of Coal Liquefaction.** As shown in the previous section, three distinct phases in the coal liquefaction process in the absence of hydrogen and a catalyst are observed. The initial rapid conversion (in the first 30 to 60 s) is due to the extraction of a soluble fraction of the coal into the processing solvent. This is followed by a pseudo-induction period and then the slow conversion of the coal structure to liquid products. This pseudo-induction period is a transition interval which is due to the simultaneous occurrence of these two processes, a very rapid extraction which is ending and a relatively slower liquefaction of the coal matrix which is becoming dominant. Based on this hypothesis, the liquefaction conversion observed in experiments, therefore, is the sum of the conversions of these two processes:

$$X = X_s + X_r \quad (2)$$

where  $X$  is the liquefaction conversion determined in the experiments;  $X_s$  is the solubilizing conversion which is due to the extraction of the soluble materials in the coal; and  $X_r$  is the liquefaction reaction conversion which is due to the chemical breakdown of the coal structure. From Eq. 2, the liquefaction rate is the sum of the derivatives of these conversions, i.e.,

$$\frac{dX}{dt} = \frac{dX_s}{dt} + \frac{dX_r}{dt} \quad (3)$$

The extraction rate could be expressed by

$$\frac{dX_s}{dt} = k_s(X_{s0} - X_s) \quad (4)$$

where  $k_e$  is the extraction rate constant;  $X_{e0}$  is the equilibrium level of extraction of coal under liquefaction conditions; and  $X_t$  is the soluble fraction at time  $t$ . The breakdown rate for the coal matrix is given by

$$\frac{dX_t}{dt} = k'_t ((1 - X_{e0}) - X_t)^\alpha C_t^\beta P_{gas}^\gamma \quad (5)$$

where  $k'_t$  is the reaction rate constant;  $X_t$  is the liquefaction reaction conversion at time  $t$ ;  $C_t$  is the tetralin concentration; and  $P_{gas}$  is the nitrogen or hydrogen pressure. When a large amount of tetralin is used in the liquefaction (for example, 8 to 1 of tetralin to coal ratio was used in this study),  $C_t$  is approximately equal to a constant.  $P_{gas}$  is held a constant during the liquefaction run in this study. Assuming  $\alpha = 1$ , Eq. 5 is simplified to

$$\frac{dX_t}{dt} = k_t ((1 - X_{e0}) - X_t) \quad (6)$$

Integrating with boundary conditions of  $X_t = 0$  and  $X_t = 0$  at  $t = 0$  and substituting  $(1 - X_{e0})$  by  $X_{\infty}$  which is defined to be the maximum conversion due to liquefaction reactions, Eqs. 4 and 6 become

$$\ln(1 - \frac{X_g}{X_{\infty}}) = -k_g t \quad (7)$$

and

$$\ln(1 - \frac{X_t}{X_{\infty}}) = -k_t t \quad (8)$$

respectively.

**Kinetics of Illinois #6 and Wyodak-Anderson Coal Liquefactions.** The plot of  $\ln(1 - X_t/X_{\infty})$  against  $t$  for the Illinois #6 coal liquefaction in tetralin under 1000 psig  $N_2$  at 390 °C is shown in Figure 2. The slope gives a measured rate constant for extraction of  $k_e = 2.81$  with an  $r^2$  of 0.97. The plot of  $\ln(1 - X_t/X_{\infty})$  against  $t$  for the Illinois #6 coal liquefaction reaction process is illustrated in Figure 3. It shows two distinct reaction stages: a rapid one with a rate constant of 0.027 for the first 5 minutes, and a slower one of 0.0054 for times greater than 5 minutes. The kinetic parameters of the Illinois #6 and Wyodak-Anderson coal liquefactions evaluated by the proposed model are summarized in Table 1. As an example, Figure 4 shows experimental data and modelling curve at the reaction times up to 10 min for Wyodak-Anderson coal liquefaction in tetralin at 390 °C under 1000 psig  $N_2$ . It shows that the model fits the experimental data very well.

Rate constants of  $k_e$  and  $k_t$  at three temperatures (358, 390, and 408 °C) were used to estimate activation energies of extraction and liquefaction reaction processes. The plot of  $\ln k_e$  against  $1/T$  and  $\ln k_t$  vs  $1/T$  shown in Figures 5 and 6 give activation energies of 14 and 22 kcal/mol for the solubilization and liquefaction reaction processes, respectively.

It is of interest to compare these results with those obtained by others at higher conversion. Wiser (2) obtained an activation energy value of 28.8 kcal/mol for Utah bituminous coal liquefaction at 63 to 94% conversion. Curran et al. (1) obtained two values for a rapid and a slow rate with mean values of 30 and 38 kcal/mol on Pittsburgh Seam bituminous coal at 2.5 minutes and 2 hours, respectively. They used a process-derived solvent from 325 to 435 °C. While the 22 kcal/mole value seems rather low, coal has obviously both weak and strong bonds which will be broken in order of their bond strength. The process derived solvent may strongly affect the relative amounts of the extraction and liquefaction stages in the Curran work. All of these values are low compared to the strength of carbon-carbon bonds and obviously the activation energies observed by us and others reflects the reaction complexity as well as the particular bonds being broken.

**The Retrograde Reactions Occurring during liquefaction.** As reported above, increasing temperature results in a levelling off of liquefaction yields due to the production of fixed carbon (FC) which results in lower liquefaction yields and production of tars and coke. Understanding this onset of retrograde reactions is of great importance for improvement of the direct coal liquefaction process. Analysis of these residues show decreasing hydrogen to carbon ratios as the coal residues are exposed to higher temperatures and longer reaction times (see Figure 7). It is not surprising therefore that introduction of a hydrogenation catalyst in the liquefaction process has a profound effect limiting the rate of formation of fixed carbon FC and therefore increasing the liquefaction yields. Interestingly, however, when a good hydrogenation catalyst is used, increasing reaction temperature up to a point actually increases yield and decreases FC formation (8).

## Summary and Conclusions

The direct liquefaction of coal shows distinct stages: an extraction stage and multiple slower stages representing the breakdown of various components of the coal structure. These only become apparent with a reactor system capable of accurately distinguishing conversions at reaction times as low as 10 seconds.

The liquefaction conversion observed in the experiments is the sum of the two simultaneous liquefaction processes of extraction and liquefaction of the coal structure. Based on this model, the liquefaction kinetics in each stage of the entire process can be adequately described.

The extraction stages in the bituminous and subbituminous coals studied to date are about two orders of magnitude faster than the structure breakdown stages and have correspondingly lower activation energies. The liquefaction of the coal structure itself also consists of multiple steps of different rate constants and activation energies.

The retrograde reactions can be followed by thermogravimetric analysis of the coal liquefaction residues. They are suppressed by catalytic hydrogenation during the liquefaction process.

## Acknowledgements

The support of this work under DOE Contract DE-PS22-93PC93201 is gratefully acknowledged.

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Table 1 The rate constants of the Illinois #6 and Wyodak coal liquefactions

Coal	T, °C	time	Liquefaction stage	Rate constant k	r <sup>2</sup>
Illinois #6	358	0 - 2 min	Extraction	0.848	0.996
		0 - 60 min	Reaction	0.00275	0.999
	390	0 - 1.5 min	Extraction	2.81	0.997
		0-5 min	Reaction (R1, fast)	0.0276	0.999
		> 5 min	Reaction (R2, slow)	0.00541	0.998
	408	0 - 1 min	Extraction	6.05	0.998
		0-10 min	Reaction (R1, fast)	0.0458	0.972
		> 10 min	Reaction (R2, slow)	0.00301	0.987
Wyodak-Anderson	390	0 - 0.5 min	Extraction	11.8	0.996
		0-15 min	Reaction (R1, fast)	0.0195	0.995
		> 15 min	Reaction (R2, slow)	0.0161	0.999

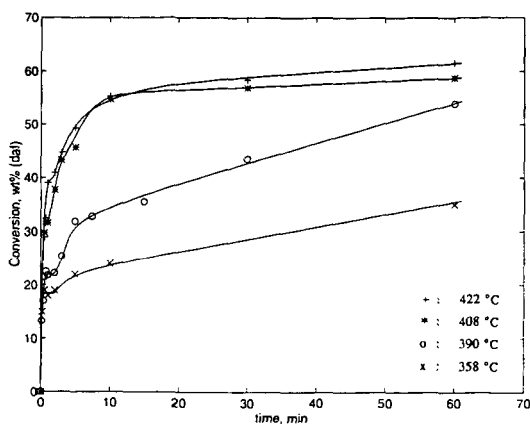


Figure 1 Conversion vs time for Illinois #6 coal liquefaction without added catalyst in tetralin (tetralin:coal = 8:1 mass ratio) under 1000 psig  $N_2$

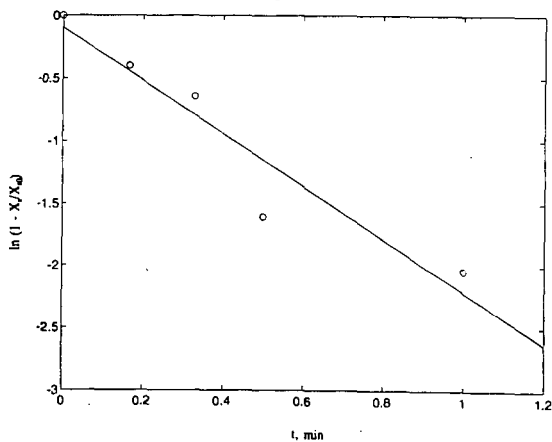


Figure 2  $\ln(1 - X_t/X_\infty)$  vs  $t$  for the Illinois #6 coal liquefaction in tetralin under 1000 psig  $N_2$  at 390 °C

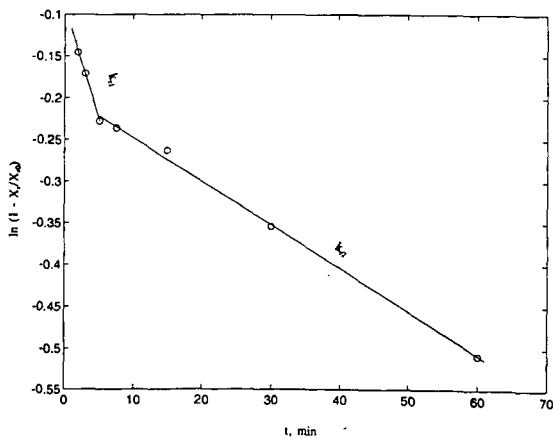


Figure 3  $\ln(1 - X_t/X_\infty)$  vs  $t$  for the Illinois #6 coal liquefaction in tetralin under 1000 psig  $N_2$  at 390 °C

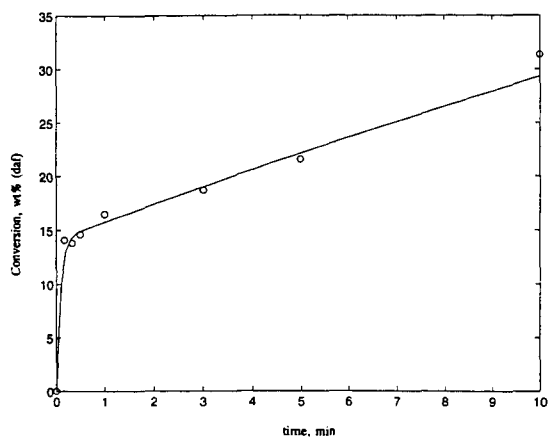


Figure 4 Plot of the experimental data and modelling curve at the reaction times up to 10 min for Wyodak-Anderson coal liquefaction in tetralin at 390 °C under 1000 psig N<sub>2</sub>.

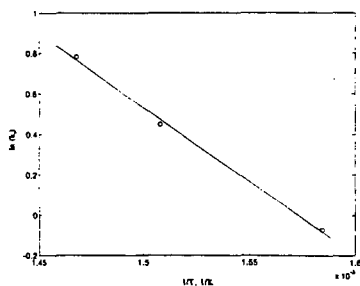


Figure 5  $\ln k$ , vs  $1/T$  for the thermal liquefaction of Illinois #6 coal (Extraction stage)

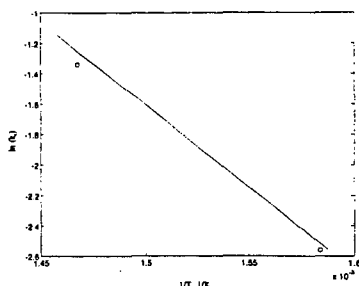


Figure 6  $\ln k$ , vs  $1/T$  for the thermal liquefaction of Illinois #6 coal (Reaction stage)

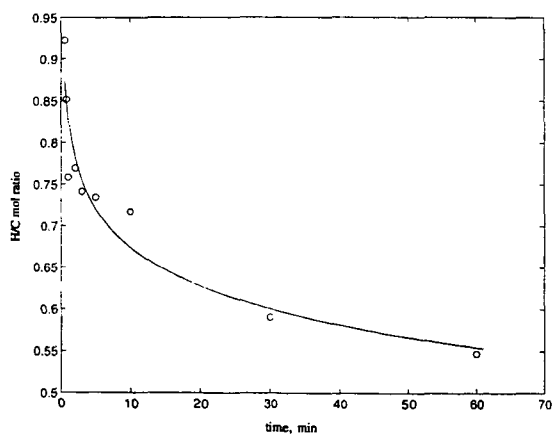


Figure 7 H/C mol ratio of the liquefaction residues of Illinois #6 coal without added catalyst in tetralin (tetralin:coal = 8:1 mass ratio) under 1000 psig N<sub>2</sub> at 422 °C